



INVESTOR IN PEOPLE

6800/02557
The Patent Office

Concept House

Cardiff Road 6 OCT 2000

Newport

South Wales

NP10 8QQ

PRIORITY DOCUMENT

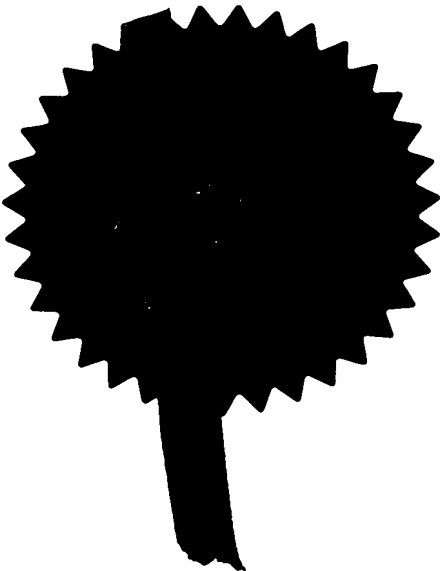
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

4
I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

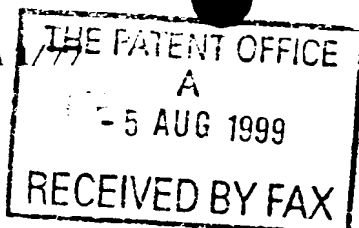
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated 2 October 2000

Patents Form

Patents Act 1977
(Rule 16)The
Patent
Office06AUG99 E467382-1 202645
P01/7700-0.00 - 9918436.8

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

P71275GB

2. Patent application number

(The Patent Office will fill in this part)

9918436.8

05 AUG 1999

3. Full name, address and postcode of the or of each applicant (underline all surnames)NATUROL LIMITED
SECOND FLOOR
BROADCASTING HOUSE
ROUGE BOUILLON
ST. HELIER
JERSEY, JE2 3ZA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

7715907006

4. Title of the invention

A NOVEL PROCESS FOR PREPARING FINE EXTRACTS
AND OILS FROM PLANTS AND OTHER MATTER

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)DIBB LUPTON ALSOP
FOUNTAIN PRECINCT
BALM GREEN
SHEFFIELD
S1 1RZ
7074917001

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description	29
Claim(s)	3
Abstract	1
Drawing(s)	1

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

DIBB LUPTON ALSOP

05.08.99

12. Name and daytime telephone number of person to contact in the United Kingdom

ATKINSON, JONATHAN
0113 241 2641

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

A NOVEL PROCESS FOR PREPARING FINE EXTRACTS AND OILS FROM
PLANTS AND OTHER MATTER

5 The present invention relates to a method of extracting
and concentrating oils from materials in which the oils
are already dispersed. More particularly, the present
invention is concerned with the extraction of fixed and
mineral oils, and/or essential oils, from materials using
a process of solvent extraction which is performed under
10 pressure.

The term "Fixed Oil" is usually used to describe oils of
vegetable or animal origin which are not volatile oils.
They routinely comprise natural mixtures of mono- di and
tri-glycerides, fatty acids, sterols (and their esters)
15 and natural waxes.

"Mineral Oil" is a term usually used to describe
petrochemical oils often derived from below ground level,
which are normally mixtures of aliphatic and aromatic
hydrocarbons of a very wide variety of chain length and
20 molecular weight. These oils are often the sources of
lubricating and fuel oils.

The term "Essential Oil" is usually used to describe
those volatile oils of low molecular weight which
incorporate the fragrance and flavour of components
25 derived from plant materials.

In an earlier application (GB2276392) we described the
use of HFC 134a (1,1,2,2 - tetrafluoroethane) as a solvent
for the extraction of essential oils from natural
sources.

2

However HFC 134a is in fact a very poor solvent for many compounds, particularly less volatile compounds. Thus, whilst HFC 134a is able to dissolve some essential oils thereby facilitating extraction of such oils from plant-based materials, this solvent is not able easily to dissolve compounds of lower volatility such as fixed oils. HFC 134a is therefore capable at ambient temperatures of extracting only very high quality fragrant and aromatic essential oils i.e. delicate oils of high volatility and low molecular weight and it will not dissolve the fixed oils which are also frequently associated with these components in the natural raw material.

Because it is a very poor solvent, large quantities of it must be used in order to obtain a commercially acceptable yield of the desirable component extracted from most raw materials.

In another unpublished application (GB 9905054.4) we describe a process in which HFC 134a is used to extract fixed and mineral oils from a substance. This process relies on the unexpected finding that raising the temperature only a few degrees Celsius results in a marked increase in the solubility of fixed and mineral oils in HFC 134a. The process is conducted in a sealed apparatus including a first vessel in which the substance is contacted with HFC 134a at an elevated temperature and second vessel in which the HFC 134a (now containing dissolved fixed or mineral oil) is cooled. The fixed or mineral is precipitated out of the solution and can easily be separated from the HFC 134a solvent which is

then recycled to minimise losses and environmental impact.

In a variation of the process described in our unpublished application GB 9905054.4, the solvent may be
5 a mixture of HFC 134a and a co-solvent in which the fixed or mineral oil to be extracted is relatively soluble. The dissolving properties of HFC 134a are significantly increased by the addition of a suitable co-solvent. Suitable co-solvents which can be added to HFC 134a may
10 be liquids at room temperature or liquefied gases and include hydrocarbons such as the alkanes, benzene and its esters, low boiling aliphatic esters such as acetates and butyrates, ketones such as acetone, methyl isobutyl ketone, methyl ethyl ketone, chlorinated, fluorinated and
15 chlorofluorinated hydrocarbons such as dichloromethane and dichloro difluoromethane, ethers and such as dimethyl ether and diethyl ether, dimethyl formamide, tetrahydrofuran, dimethyl sulphoxide, alcohols such as methyl alcohol, ethyl alcohol, n-propanol, iso-propanol,
20 acids such as acetic acid, formic acid and even acetic anhydride, nitriles such as acetonitrile (methyl cyanide), anhydrous liquefied ammonia and other liquefied gases such as sulphur dioxide, nitric oxide, nitrogen dioxide, nitrous oxide, liquefied hydrogen sulphide,
25 carbon disulphide, nitromethane, and nitrobenzene and anhydrous ammonia could all be used in this process.

The most useful co-solvents have proved to be butane and dimethyl ether. Regrettably, though many of the useful co-solvents which are mixed with HFC 134a re-confer the
30 serious hazard of flammability on the mixtures and

therefore raise safety issues. There may, depending on the choice of co-solvent, be other problems such as environmental issues.

5 Although it is neither a serious ozone depleter nor a VOC, unfortunately HFC 134a is a potent and powerful green-house gas. It has a global warming potential or green house gas effect some 8 times as strong as carbon dioxide. It is very chemically inert and persist in the environment for very long periods of time, during its
10 decomposition. It has a $t_{1/2}$ life between 8.6 and 16.7 years.

Historically solvents such as hexane, petroleum fractions, benzene, methylene chloride (dichloromethane) have been widely used to extract oils from an enormous
15 range of flavoursome oleo-resins, drug-containing extracts and fragrant raw materials ("concretes"). These solvents are also in common use in the engineering, petroleum and mineral industries, where they are often used to de-grease materials containing or coated in oil
20 and to clean metal parts, by the removal of oily lubricating preparations. Useful amounts of oils have even been extracted from mineral raw materials such as oil shales and tar sands with such solvents. Even soils contaminated with oily industrial waste may be remediated
25 with such solvents.

As they are all highly flammable, one disadvantage of conventional solvent systems such as hydrocarbon solvents, for example hexane and benzene and petroleum fractions, has always been the dangers of fire or
30 explosion and incineration. These solvents also present

5

further hazards to the operators of such processes because many hydrocarbon and chlorinated solvents are harmful or toxic by inhalation and ingestion. They are frequently carcinogenic and all of the hydrocarbon solvents used in current practice are classed as VOCs (volatile organic compounds) which are said to have a positive photo-chemical ozone generating potential.

A further disadvantage of the most commonly used solvents, hexane and "petroleum ether", is that their boiling points (at atmospheric pressure) are in excess of 50 degrees Celsius. Hence, in order to remove such solvents from the solutions of the desired components, the desired component must either be exposed to high temperatures or high vacuum. Both of these treatments detract from and are damaging and deleterious to the quality of the desired component or extract. Also, the evaporation of the solvent from the solution of the oil, and the solvent recovery by condensation is expensive on account of the energy costs.

The finished product from such processes are often intended for public consumption and the presence of toxic or harmful residues may present difficulties when seeking regulatory approval of the finished product.

These problems become even more serious when (as is increasingly the case) statutory authorities are demanding that the solvent residue levels in oils sold for use in human food stuffs are required to meet increasingly stringent requirements such as occurrence only at 50, 10 and even 1 part per million. Achieving such low levels of solvent residue require that the

solution and extract be exposed to very high vacuum and/or very high temperatures. Such treatment can result in serious loss of the precious volatile components from the extracts and serious thermal damage to the desirable
5 component.

A strategy to overcome these problems has been to employ hydrocarbon solvents such as butane and even propane (in liquid form under pressure). However, these processes are even more dangerous, of course, as any leakage of the
10 (usually odourless) solvent vapours from the operating equipment, poses a greatly enhanced risk and chance of explosion and incineration.

The use of less flammable solvents such as chlorinated hydrocarbon solvents has gone some way to reducing these
15 risks. For example, the use of methylene chloride (dichloromethane) to extract valuable components such as caffeine from coffee and tea has become common. Similarly, perchloroethylene has a long history of use in the dry cleaning industry to de-grease oily clothing.

20 However, many of the traditional chlorinated solvents present their own problems. Most of these materials are either harmful or toxic or may be damaging to the environment. Their vapours are believed to deplete the protective ozone in the stratosphere. Many of these
25 chlorinated solvents are also green-house gases and may lead to global warming.

The process we now describe in this specification is of great value in the extraction of high quality, desirable components such as oils, pigments, pharmacologically

active ingredients and resins from a wide range of plant, animal and mineral matter, of both terrestrial and marine origin. The same process, when using the solvent systems according to an embodiment of the invention is able to
5 extract fixed and mineral oils.

The process comprises the contacting of a bulk raw material in which the desired component is already contained, with a solvent so as to allow the desired component to dissolve in the solvent. It provides for
10 the removal of the and separation of the solution of the desired component in the solvent, from the bulk raw material. It further provides for the removal of the solvent from the solution and its recovery for re-cycling and re-use, and for the harvesting of the solute from
15 which the solvent has been removed. The solute - in such cases - comprises the desired component.

The extraction of desirable components from bulk raw materials using these processes must be carried out in sealed (pressure vessel) equipment. It is highly
20 desirable to collect as much of the used solvent from the solution formed (of the solvent and the desirable component) and from the spent and extracted bulk raw material. Nevertheless, it is inevitable that some loss of solvent vapour into the atmosphere always occurs.

25 This consideration has lead us to search for a solvent which has more acceptable physiological and environmental characteristics and which is also an effective solvent capable of extracting fixed, mineral and essential oils.

The present invention thus aims to provide an economical process which is also able to provide the extracted oils in relatively high yield. It is also an aim to provide a quick extraction process which can be used commercially.

- 5 It is also an aim to provide a process which is easy to run and which does not require bulky or complicated apparatus. It is another aim to use a solvent which is not environmentally damaging and which does not have any significant photochemical ozone generating potential.
- 10 Such a process aims to eliminate or reduce the losses of solvent during the extraction process. Indeed, it is a further aim to provide a process in which solvent losses are minimised so that there is substantially 100% solvent recovery.
- 15 It is also an aim to avoid the risk of fire or explosion by using a non-flammable solvent system, or at least a system having a significantly reduced risk of fire or explosion.

20 It is also an aim to achieve a reduction in the or the absence of any toxic solvent residues in the final product. It is an aim that the extracted oil be substantially free of traces of solvent so that the extracted oil may easily satisfy any present or future regulatory requirements.

- 25 It is also intended to dispense with the need for the elimination of or evaporation and condensation of large quantities of solvents.

We have found that iodotrifluoromethane (ITFM) satisfies most or all of these requirements.

According to one aspect of the present invention, there is provided a method of extracting oil from a substance, the method comprising the steps of:

- 5 a) contacting the substance with a solvent comprising iodotrifluoromethane and optionally one or more co-solvents, in a first sealed vessel;
- 10 b) optionally causing agitation and/or heating of the mixture of the solvent and the substance;
- 15 c) separating the resulting solution from the substance by transferring the solution to a second vessel and optionally cooling the separated solution; and
- 20 d) removing the iodotrifluoromethane together with any optional co-solvent from the second vessel so that the desired oil remains in the second vessel substantially free of solvent.

Iodotrifluoromethane has the advantage that it has no global warming potential and is not a VOC. It is not flammable and is actually used as a fire extinguisher. It does not deplete the ozone layer, is effectively non-toxic and represents virtually no biological hazard or environmental threat. It has a very low boiling point (-22.5 degrees Celsius at atmospheric pressure) and a modest vapour pressure of only 63.7 psi (4.3 Bar) at 25
30 degrees Celsius.

10

It is an excellent extraction medium and solvent for many oils including triglycerides, fatty acids, sterols and their esters, natural waxes, hydrocarbons (both straight and branched chains and cyclic and poly-cyclic) with
5 molecular weights up to several hundreds. It also dissolves fragrance oils, pigments, flavour oils and many pharmaceutical components from natural plant and animal raw materials. In this embodiment of the invention, it is not usually necessary to perform heating in step (b)
10 of the process.

It presents no special problems in handling and recovery for re-cycling.

Although it is currently a costly solvent, the financial penalty attendant on its use may be minimised using the
15 process of the present invention since almost complete solvent recovery occurs. Furthermore, the solvent offers tremendous advantages to the environment.

Because it has a low boiling point, extraction of and recovery of desirable components can be carried out at
20 room temperature or below, thus eliminating any chance of the thermal degradation or damage to the extracts that often occurs when other solvents are used. Iodotrifluoromethane (ITFM) is pH neutral and does not hydrolyse appreciably in water at room temperature.

25 Should it be necessary to reduce the wide spectrum of solutes which dissolve in iodotrifluoromethane (ITFM) (i.e. to render it more selective), it can be mixed with one or more poor or non-solvents. Suitable poor solvents or non-solvents are for example, HFC 134a 1,1,1,2-

11

tetrafluoroethane) or HFC 4310 (1,1,1,2,2,3,4,5,5,5-decafluoropentane). This may be done to impart selectivity on the extraction process in order to enhance the amount of a particular oil in a mixture of extracted
5 oils. In this case, since the co-solvent (such as HFC 134a) only represents a part of the solvent rather than being the solvent any problems which may be associated with the co-solvent itself are minimised.

An embodiment of the invention thus makes use of the
10 property of mixtures of ITFM and one or more suitable co-solvents to dissolve to specified and finite limits of molecular weight or polarity. This confers a degree of selectivity on the solvent mixtures to extract components of specified molecular weight, such as volatile
15 components of fragrance oils, whilst excluding from solution many of the materials which would then be considered to be undesirable contaminants, such as triglycerides, fatty acids and natural waxes. It is, however, important that the presence of the co-solvent
20 does not lead to a solvent system which is toxic or hazardous to health.

A related embodiment of this invention also makes use of the observation that certain mixtures of ITFM with one or more suitable co-solvent do not dissolve fixed oils such
25 as triglycerides, fatty acids, natural waxes, mineral oils and petroleum fractions etc at low temperatures. At elevated temperatures, such solvent mixtures do in fact dissolve these materials. Hence it becomes a simple matter to dissolve such fixed and mineral oils and
30 extract them from the bulk raw material in which they

12

occur by heating the solvent mixture in the presence of the substance. Removal of the hot solution and cooling it causes the solutes to precipitate from solution in all cases, the solutes (being of lower specific gravity than the solvent) float to the top of the cooled solution and can be easily harvested. In this case, the method would involve both the step of elevating the temperature in step (b) and the step of cooling in step (c) the separated solvent solution once it has been transferred to the second vessel so as to release any dissolved oil. At this point, either the released oil or the iodotrifluoromethane solvent can be removed from the second vessel to complete the separation.

The invention also relates to an apparatus for performing oil extraction.

According to another aspect of the present invention, there is provided a sealable apparatus comprising first and second vessels, each vessel having at least one closable valve through which solvent may pass, wherein the first and second vessel are in fluid communication with one another by means of the closable valves, wherein the first vessel is adapted to receive a substance from which oil is to be extracted and incorporates on the or each valve a filtering device to prevent passage of the substance out of the first vessel through the or each valve, and wherein a solvent comprising iodotrifluoromethane together with one or more optional co-solvents is provided in the first vessel and may be transferred between the first and second vessels via the or each valve.

In an embodiment, the or each valve is a one way valve and the first and second vessels each have an inlet valve and an outlet valve, the apparatus being arranged in the form of a circuit so that the outlet valve of the first
5 vessel is connected to the inlet valve of the second vessel, and the outlet valve of the second vessel is connected to the inlet valve of the first vessel, wherein the flow of solvent around the circuit occurs in one direction only.

10 In another embodiment, the first vessel is provided with a heating means and/or is associated on its inlet side with means for heating incoming solvent.

In a further embodiment, the second vessel is provided with cooling means and/or is associated on its inlet side
15 with means for cooling incoming solution.

In a further embodiment the apparatus includes a reservoir of additional solvent and means for introducing to or removing solvent from the circuit. Preferably, the point of addition or removal of solvent from the circuit
20 is between the outlet side of the second vessel and the inlet side of the first vessel.

In another embodiment, the apparatus includes means for withdrawing from the second vessel directly and/or from the inlet side of the second vessel oil which has
25 separated from the solvent.

In a further embodiment, the apparatus includes means for determining the pressure in the circuit and/or the temperatures of the first and second vessels.

14

In a further embodiment, the first and second vessels are transparent pressure vessels capable of withstanding pressures of not more than 25 bar.

5 The appropriate co-solvent and iodotrifluoromethane: co-solvent ratio for a given substance is determined as follows.

10 An empty bottle together with a removable seal is weighed and the weight recorded (Weight A). This assembly should be designed to be able to withstand a pressure of say 10 BarG.

Into the bottle is placed a sample of the substance i.e. the oil-containing raw material to be extracted, or a sample of the oil itself.

15 The bottle and seal is weighed again and the weight recorded (Weight B). The bottle is then closed and sealed. The difference between weight B and A is the weight of the solute containing oil or the oil.

20 The iodotrifluoromethane alone is introduced into the bottle and the mixture shaken until the contents are homogenous and the solute is in complete solution. The bottle and contents are weighed again and the final weight of the bottle and contents are recorded (Weight C). The difference between Weight B and Weight C is the weight of the added iodotrifluoromethane.

25 Co-solvent in which the solute is only poorly soluble or in which it is insoluble is then progressively introduced into the bottle. At first no obvious change takes place, but as the quantity of co-solvent is increased, the

15

contents of the bottle will be seen to turn from crystal clear to opalescent. The weight of the bottle and contents is again recorded (Weight D). The difference between Weight D and Weight C is the quantity of co-solvent added.

In order to ensure that the precipitation of oil from the mixture has reached its optimum, the bottle may now be placed in a refrigerator, whereupon the contents will at first become cloudy and soon a clear and distinct layer of oil will separate and float on the lower layer of clear solvent. The solvent at low temperature can then be withdrawn and introduced to another bottle charged with more of the oil or the oil-containing raw material. This cold solvent will not dissolve the oil, but on warming, it will be seen to form a homogeneous solution (which will itself separate again into two layers on cooling).

This procedure will allow calculation of the composition of a solvent mixture. For example: The total weight of solvent used is $D - B$. the weight of iodotrifluoromethane is $C - B$ and the weight of co-solvent is $D - C$.

Hence the weight % composition of the mixed solvent is:

$$\begin{aligned}\text{iodotrifluoromethane} &= (C - B / D - B) \times 100\% \\ \text{co-solvent} &= (D - C / D - B) \times 100\%\end{aligned}$$

25

The % concentration of solute in the solution

$$= (B - A / D - A) \times 100\%$$

16

The invention will now be described with reference to Figure 1 which shows an apparatus suitable for continuous extraction of fixed and mineral oils according to one embodiment of the process of the present invention.

5 Two vessels (1) and (2) equipped with closeable valves were coupled together via two sets of tubing (3, 4). Both vessels are capable of withstanding pressure typically up to 25bar. Below vessel (1), the tubing (3) was in the form of a coil (5) sitting in a bath of liquid
10 (6) which could be heated and maintained at a pre-selected temperature. The coil of tubing (5) could, however, be heated by another means or vessel (1) could be heated directly.

Vessel (1) was equipped with internal filters (7) at both
15 ends, whereas vessel (2) was equipped with a filter (8) only at the lower end.

The second vessel (2) was surrounded by coils (9) containing a flow of cooling liquid and the outside of the coils was insulated. Other means of cooling vessel
20 (2) could also be used, for example a stream of cooling gas or a cooling bath.

The circuit was furnished with an inlet (10) and outlet (11) valves for solvent. During operation of the equipment, the inlet valve was coupled to a solvent
25 reservoir (12) which could be used to both fill and the system with solvent and maintain the level of solvent during operation. Outlet valve (11) was provided to enable the system to be drained.

17

At the top of vessel (2), a valve (13) is fitted to facilitate the recovery of oil when this becomes necessary or desirable. A pressure gauge (16) may be provided in the circuit.

- 5 The same equipment can be used regardless of whether the solvent is iodotrifluoromethane alone or in combination with a co-solvent, and regardless of whether any heating or cooling is actually performed.

10 The operation of the equipment is for the purpose of illustration only described as follows in relation to a mixture of iodotrifluoromethane and a co-solvent to extract a fixed oil:

1. Vessel (1) (which has removable end caps) is charged with the material from which oil is to be extracted
15 (usually in the form of a finely divided particulate solid). The end caps and filters are then replaced. The vessel is then connected to the remainder of the equipment. Air is then removed from the sealed equipment at this stage.
- 20 2. The equipment (now fully sealed) is then fully charged with solvent from the bulk solvent storage tank (12) (which remains connected to the equipment throughout the operation).
3. The heating bath (6) is then filled with water or
25 oil and the heating means turned on if required.
4. Cold liquid or gas is circulated round the cooling coils (5) causing the temperature of the second vessel (2) (and its contents) to cool if required.

As the temperature of the liquid in the heating bath rises, so does the temperature of solvent in the tube below vessel (1). This, of course, causes hot solvent in vessel (1) to rise through the contents of the vessel (1) due to natural convection. The contents of vessel (1) are restrained inside vessel (1) by the filters (7) disposed at the top and bottom. The liquid displaced upwards is replaced by cold liquid falling through vessel (2) due to convection.

10 The entire liquid in the circuit thus becomes mobile and circulating. As hot liquid passes up through the contents of vessel (1) oil is extracted from the solid material. As the solution enters the top of vessel (2) it is cooled and its solute (the oil) precipitates out of
15 solution.

Alternatively, in the absence of heating and the resulting convection currents which occur, the solvent may be pumped around the circuit.

Because the oil is lighter than the solvent, it floats to the top of vessel (2) and collects there as it is not able to pass out of the bottom of vessel (2).

When it is considered that sufficient oil has been extracted, all the valves are closed except valves (14) (the inlet valve for vessel (2)) and valve (15) (the outlet valve for vessel (2)). Valve (13) is then opened to release the oil and the oil can be decanted into a bottle.

19

The system may be emptied after use by allowing solvent to drain out of valve (1) into a suitable container for re-cycling and recovery by evaporation.

5 It will be immediately apparent to one versed in the art, that this process is capable of producing oil without any evaporative step. Since evaporation of the solvent is one of the major costs involved in more traditional methods of extraction, this constitutes a major improvement in the extraction of such oils and represents
10 a significant cost saving.

Since iodotrifluoromethane is neither flammable, nor toxic, nor environmentally damaging and (in normal operation) is never released into the environment, the process of the present invention represents a significant
15 improvement over current technologies.

In another embodiment of the process (not shown), the apparatus comprises two sealable vessels (which are preferably transparent and made of strengthened or reinforced glass) each being capable of withstanding a
20 pressure of up to 20 bar or even 25 bar. Each vessel is equipped with a closeable valve which acts as an inlet and an outlet valve. One vessel is also equipped with a removable filtering device, such as a wire gauze or wire wool to prevent the exit of raw material from the vessel
25 at the same time as the solvent is withdrawn.

The two vessels are connected to each other via their inlet/outlet valves so as to form a sealed unit. Typically each vessel is 50mls to 2000mls capacity, and preferably 100mls to 500mls. Such an apparatus is easily

20

assembled and handled. However, there are no particular limitations other than the usual practical limitations, on the upper size of such apparatus.

5 In another embodiment (not shown), it is possible to extract a fixed or mineral oil from a substance in an apparatus comprising two vessels which is not arranged in the form of a circuit. The raw material is placed in a first vessel and the extraction medium (ie the solvent) is also introduced into the first vessel. The
10 inlet/outlet valve of both vessels are then closed and the ensemble is warmed, typically to 40°-60° (and preferably not more than 50°C), in an oven or using other suitable heating means. The apparatus may be agitated during heating or may contain agitation means such as a
15 magnetic flea.

After an appropriate residence time at the elevated (holding) temperature, typically in the range 1 to 20 minutes and preferably in the range 3 to 8 minutes from the point of view of efficiency and cost effectiveness,
20 the solution is transferred from the first vessel to a second vessel and the ensemble is cooled to room temperature or lower. Ideally, the ensemble is cooled to a temperature in the range -10° to 25°C and preferably in the range 0° to 20°C. Cooling below -10°C is possible
25 but increases the costs and complexity of the process.

Transfer of the solution is achieved via the inlet/outlet valves and the raw material remains in the first vessel on account of the filter. The valves are closed following transfer of the solvent and before cooling is
30 commenced.

21

On cooling, the extracted oil precipitates out of solution and begins to aggregate. Since the extracted oil is invariably significantly less dense than the solvent medium the extracted oil floats on the top of the solvent layer as a separate immiscible/insoluble layer. The extracted oil can thus be easily separated by decanting. The solvent, which is almost entirely free of the oil, can then be returned to the first vessel for use in a further extraction cycle. This process can be repeated several times if desired. From a practical point of view, 10 cycles is the upper limit with 3 to 5 cycles being preferred on the basis of efficiency and time.

This manual procedure, though highly effective, was somewhat tedious to carry out and the whole process is preferably performed as a continuous operation as described above.

Temperature difference between vessels (1) and (2)

For maximum economic use of equipment designed to prepare extracts such as fixed or mineral oils, it is beneficial to operate vessels (1) and (2) at widely dissimilar temperatures. (The difference between these temperatures is commonly referred to as " ΔT "). The larger the " ΔT " the better the equipment will perform.

However, limits on " ΔT " are imposed by the design and fabrication of the equipment.

Upper limit of operating temperature of Vessel (1)

22

When iodotrifluoromethane is used, whether mixed with another solvent or not, a rise in the temperature of operation of Vessel (1) will automatically cause an increase in the pressure (vapour pressure) within the sealed system. Indeed, the highest operating temperature of vessel (1) must obviously never exceed and be less than the "critical temperature" of the solvent (mixture) in use.

Also this highest operating temperature would be limited to a temperature above which damage to the raw-material or the extract might occur.

Lower limit of operating temperature of Vessel (2)

The operating temperature of Vessel (2) must be as low as can be conveniently arranged. Sub-ambient and even refrigeration temperatures can be used.

The lower limit of operation of Vessel (2) will be determined by the characteristics of the solution (and its ability to dissolve solute). The solute must dissolve in the solvent as "poorly" as can be arranged and the "poverty" of this dissolution can be enhanced by lowering the temperature of operation of Vessel (2). The low limit is also governed by the viscosity of the resulting oil since at very low temperatures some oils may become difficult to handle.

The operation of the equipment is described for the purpose of illustration only as follows in relation to the extraction of an essential ie volatile oil: the substance containing the essential oil is introduced into an extractor, having the shape of a flanged tube and

furnished with removable end caps, each of which comprises a plate and a sheet of stainless steel mesh secured thereon to form a filter. The end caps or plates are also equipped with a port which is capable of closure
5 and through which both gases and liquids can pass via the stainless steel filter mesh.

The extractor is closed and air is pumped out to a pressure of less than 40mbar. A source of supply of liquid iodotrifluoromethane is connected to the extractor
10 and liquid solvent is allowed to pass to the extractor. The contents of the extractor are thus bathed in iodotrifluoromethane. The extractor is then sealed as the source of iodotrifluoromethane is disconnected. The
15 extractor is then tumbled on its lateral axis for a period of time to ensure intimate contact between the solvent and the substance.

After the tumbling has stopped, the outlet is connected via alternative pipework to a small evaporator which has previously been evacuated to a pressure of 40mbar. The
20 solution of oil in the iodotrifluoromethane solvent is allowed to pass intermittently from the extractor into the evaporator, to retain a level of liquid and gas filled headspace in the evaporator. The evaporator is
25 then connected to the inlet of a compressor which is allowed to withdraw iodotrifluoromethane gas from the head space of the evaporator and to compress the gas (on its outlet side) to a pressure in excess of 5 bar.

At this pressure, and at room temperature, the gas is reliquefied and can either be recycled to the extractor
30 to flush out residual oil or be reintroduced to the

original reservoir of solvent for re-use on a further bath.

Inevitably, during this process the evaporator cools to very low temperatures and it is desirable to immerse it
5 in a water bath furnished with an immersion heater and a thermostat. The thermostat can be set to activate the immersion heater when the water temperature falls to for example 10°C and to switch off the heater whenever the temperature of the water exceeds for example 12°C. In
10 this manner, the evaporator may be operated at about 10°C and the vapour pressure is 1 to 3 bar at the compressor inlet.

The pressure contained the evaporator throughout this process is in the region of 30 psi. Once all the
15 solution has passed from the extractor to the evaporator, and all the solvent from both the extractor and the evaporator has been evaporated, the vapour pressure inside the evaporator begins to fall.

When this pressure had fallen to just above 0 psig an
20 outlet on the bottom of the evaporator is opened so the oil solute (the extract) can run into a suitable receptacle. Weighing of the receptacle before and after the introduction of the oil reveals the yield of fragrant oil.

25 Following the removal of the oil, the compressor can be allowed to continue to suck residual solvent vapour from the extractor and from the substance within it. By the time the pressure within the extractor has fallen to

25

100mbar over 99.9% of the iodotrifluoromethane solvent will have been returned to the original reservoir.

To improve the recovery of solvent the extractor and its contents can be heated.

- 5 The present invention will now be illustrated by means of the following examples.

EXAMPLE 1

At an ambient temperature of 20 degrees Celsius, 140 grams of peanut oil were introduced into a PET bottle of capacity 2500 ml and designed to withstand 10 BarG. The bottle was fitted with an aerosol valve. This oil was dissolved in 780 grams of iodotrifluoromethane which was introduced into the bottle, via the aerosol valve, from a bulk container.

- 15 The solution formed was crystal clear and pale yellow in colour. It formed a completely homogeneous solution, a single phase.

HFC 134a was then introduced into the bottle via the aerosol valve from a similar bulk storage container, until the mixture separated into two distinct layers. The bottle was weighed to ascertain how much HFC 134a had been added. This proved to be 440 grams of HFC 134a. The upper layer of the two phase system was yellow and clear. The lower layer was clear and water white.

- 25 Warming this two phase mixture to 42 degrees Celsius with gentle agitation for a few seconds, caused it to become clear. It formed a single phase homogeneous solution.

26

Upon cooling, a two phase system re-formed, with the yellow layer lying on top of a clear water white layer.

The composition of the solvent in this case was 36.1% HFC 134a:63.9% ITFM w/w.

5 **EXAMPLE 2**

At an ambient temperature of 20 degrees Celsius, 140 grams of peanut oil were introduced into a PET bottle similar to that of Example 1. On this occasion, 810 grams of iodotrifluoromethane was introduced into the
10 bottle via the aerosol valve. A yellow, bright homogeneous solution was obtained.

On this occasion, 440 grams of HFC 134a were introduced into the bottle. The contents of the bottle remained as a single phase, slightly opalescent solution.

15 Cooling this solution to 4 degrees Celsius caused it to separate into a "two phase" system. The upper layer being yellow and the lower layer being clear and water white. Allowing this mixture to warm to room temperature (20 degrees Celsius) with gentle agitation, caused the
20 two phase mixture to revert to its original state as a single phase, homogenous (if slightly opalescent) solution.

The composition of the solvent in this case was 35.2% HFC 134a:64.8% ITFM w/w.

25 **EXAMPLE 3**

224 grams of finely ground sesame seeds were introduced into a 2500 ml capacity PET bottle fitted with an aerosol

27

valve, at an ambient temperature of 20 degrees Celsius.
780 grams of iodotrifluoromethane was introduced to the
bottle via the aerosol valve from a bulk container.

5 Shaking the bottle caused a distribution of the sesame
seed paste. The bio-mass floated to the top as the
specific gravity of the ITFM is close to 2.0.

10 To this mixture was added 480 grams of HFC 134a. Placing
this mixture in the fridge at 4 degrees Celsius caused
agglomeration of the bio-mass. A single lump of solids
was obtained which could not be easily broken up with
shaking. This was assumed to be due to the precipitated
oil and sesame seed bio-mass becoming re-mixed.

15 Allowing this mixture to warm to room temperature caused
re-dissolution of the oil and the sesame seed bio-mass
was then much easier to disperse in the liquid.

The liquid phase of this mixture was harvested by
inverting the bottle, via a filter attached to the
aerosol valve, into a second PET container. A clear
homogeneous liquid was obtained.

20 Refrigeration of this liquid caused it to separate into
two layers. Both layers could be harvested separately
(by inverting the bottle) and the lower layer was found
to contain mostly solvent whilst the upper layer
comprised mostly oil (with a little solvent dissolved in
25 it).

The composition of the solvent in this case was 38% HFC
134a:62% ITFM w/w.

28

EXAMPLE 4

20 grams of peanut butter (Sun Pat) were introduced into a 210 ml capacity PET bottle fitted with an aerosol valve and filter. 195 grams of ITFM were added. The mixture
5 formed a cream coloured, even dispersion. 101 grams of HFC 134a were then added and the mixture shaken. The solution was filtered into a new PET bottle. 274 grams of solution were recovered.

To this solution was added a further 7 grams of HFC 134a.
10 It remained as a single phase.

A further 5 grams of HFC 134a were added. The mixture was now refrigerated and two distinct layers formed. The lower layer of this solution was recovered and added to a further 141 grams of peanut butter at 20 degrees Celsius.
15 A milky even dispersion of creamy coloured peanut bio-mass was formed. This mixture was again filtered back into the bottle in which the solution had originally been filtered and the combined filtrates were again refrigerated.

20 Refrigeration of this solution caused a great deal of oil to precipitate out of solution and a thick layer of yellow oil formed on the surface. This oily material was easily recovered by inverting the bottle following the removal of the lower (largely solvent) layer.

25 The composition of the solvent in this mixture was 37% HFC 134a:63% ITFM w/w.

EXAMPLE 5

28 grams of ground roasted cocoa beans were placed into a
210 ml capacity PET bottle and an aerosol valve with
filter was attached. 189 grams of ITFM were added and
5 106 grams of HFC 134a.

The mixture was filtered into a second bottle and
refrigerated to minus 10 degrees Celsius. White, solid,
cocoa butter was seen to rise to the surface. Re-warming
of this bottle to room temperature caused the cocoa
10 butter to melt, re-dissolve and become homogeneously
distributed throughout the liquid phase.

The composition of the solvent in this mixture was 36%
HFC 134a:64% ITFM w/w.

The present invention thus addresses many of the
15 disadvantages discussed above and provides a means of
obtaining fixed oils and mineral oils in good yields in a
form approaching 100% purity.

Claims

1. A method of extracting oil from a substance, the method comprising the steps of:
 - 5 (a) contacting the substance with a solvent comprising iodotrifluoromethane and optionally one or more co-solvents, in a first sealed vessel;
 - 10 (b) optionally causing agitation and/or heating of the mixture of the solvent and the substance;
 - (c) separating the resulting solution from the substance by transferring the solution to a second vessel and optionally cooling the separated solvent; and
 - 15 (d) removing the iodotrifluoromethane together with any optional co-solvent from the second vessel so that the desired oil remains in the second vessel substantially free of solvent.
- 20 2. A process as claimed in claim 1 wherein the co-solvent is present and is selected from HFC134a or HFC4310.
- 25 3. A sealable apparatus comprising first and second vessels, each vessel having at least one closable valve through which solvent may pass, wherein the first and second vessel are in fluid communication with one another by means of the closable valves, wherein the first vessel is adapted to receive a substance from which oil is to be extracted and

31

5 incorporates on the or each valve a filtering device to prevent passage of the substance out of the first vessel through the or each valve, and wherein a solvent comprising iodotrifluoromethane together with one or more optional co-solvents is provided in the first vessel and may be transferred between the first and second vessels via the or each valve.

10 4. An apparatus as claimed in claim 3, wherein the or each valve is a one way valve and the first and second vessels each have an inlet valve and an outlet valve, the apparatus being arranged in the form of a circuit so that the outlet valve of the first vessel is connected to the inlet valve of the second vessel, and the outlet valve of the second vessel is connected to the inlet valve of the first vessel, wherein the flow of solvent around the circuit occurs in one direction only.

20 5. Apparatus as claimed in claim 3 or 4, wherein the first vessel is provided with a heating means and/or is associated on its inlet side with means for heating incoming solvent.

25 6. Apparatus as claimed in claim 3, 4 or 5, wherein the second vessel is provided with cooling means and/or is associated on its inlet side with means for cooling incoming solution.

7. Apparatus as claimed in any of claims 4 to 6, wherein the apparatus includes a reservoir of additional solvent and means for introducing or removing solvent from the circuit.

32

8. Apparatus as claimed in claim 7, wherein the point of addition or removal of solvent from the circuit is between the outlet side of the second vessel and the inlet side of the first vessel.
- 5 9. Apparatus as claimed in any of claims 3 to 8, wherein the apparatus includes means for withdrawing from the second vessel directly and/or from the inlet side of the second vessel oil which has separated from the solvent.
- 10 10. Apparatus as claimed in any of claims 3 to 9, wherein the apparatus includes means for determining the pressure in the circuit and/or the temperatures of the first and second vessels.
- 15 11. Apparatus as claimed in any of claims 3 to 10, wherein the first and second vessels are transparent pressure vessels capable of withstanding pressures of not more than 25 bar.

33

ABSTRACT

The invention relates to a process for extracting fixed and mineral oils, and/or essential oils, from materials using a process of solvent extraction which is performed under
5 pressure. The solvent is iodotrifluoromethane or iodotrifluoromethane in combination with a co-solvent.

The invention also relates to an apparatus for performing the extraction of fixed and mineral oils, and/or essential oils.

10 Substantial reductions in or elimination of the normally high latent heat of solvent evaporation may also be achieved simply by raising or lowering the temperature of or simply by adding or removing "sensible" heat from the solvent at appropriate points during its re-circulation.

15

LDSDP\P71275.GB (ja\caw)





1977

Notes

